Phonons and Thermal Transport in Carbon Nanotube Systems

An informal review

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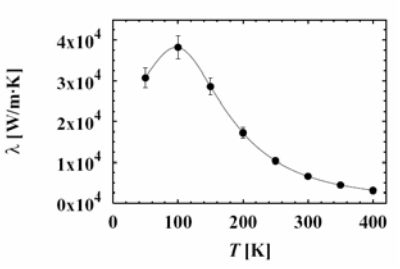
DARPA DSRC Nanoscopic Phonon Engineering Workshop
May 9, 2005

"What's the buzz?" – Great Promise:

"Due to the combination of a high speed of sound, hard optical vibration modes and a large phonon mean free path, carbon nanotubes prove to be the most efficient thermal conductors." (*D. Tomanek, 2005*)



In MD simulations of *Tomanek's* group (*2000*), the peak therm. cond. of (10,10) **SWNT** found to be 37000 W/m·K, on par with the highest value ever observed in a solid (diamond). RT value of 6600 W/m·K is also very high…

"The stiff sp^3 bonds, resulting in a high speed of sound, make monocrystalline diamond one of the best thermal conductors. An unusually high thermal conductance should also be expected in carbon nanotubes,which are held together by even stronger sp^2 bonds…

The rigidity of nanotubes, combined with a virtual absence of atomic defects or coupling to soft phonon modes of the embedding medium, should make these systems very good candidates for efficient thermal conductors".

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
09 MAY 2005	**N/A**	**-**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Phonons and Thermal Transport in Carbon Nanotube Systems	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Department of Physics The University of Texas at Dallas**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM001801., The original document contains color images.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**UU**	**13**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

But can we measure and utilize it?

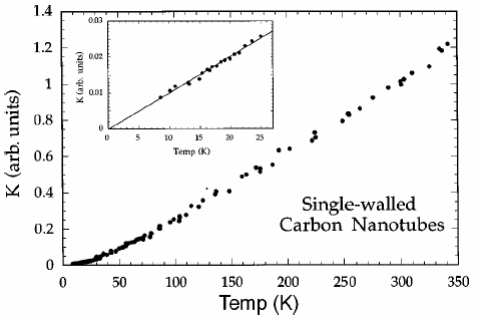
• “The expected high thermal conductivity value in nanotubes makes its direct experimental observation very difficult. Since thermal transport is likely to be dominated by phonon scattering in the contact region, the most important and currently unsolved challenge is to reproducibly create and characterize thermal contacts to a nanotube. Even if thermal scattering in the contact region could be minimized, the net thermal transport would still be limited by that of the leads”. (*D. Tomanek, 2005*)

• “Interlayer interactions quench the thermal conductivity … by nearly 1 order of magnitude. We should expect a similar reduction of the thermal conductivity when … nanotubes form a bundle or rope, become nested in multiwall nanotubes, or interact with other nanotubes in the “nanotube mat” of “bucky paper”. (*Berber, Kwon and Tomanek, 2000*)

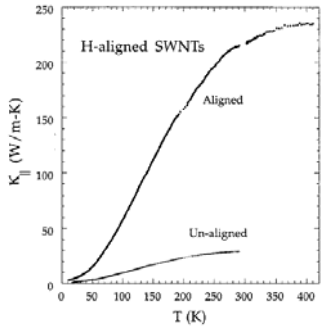
In fact, even experimental data are relatively scarce

Some “standard” references

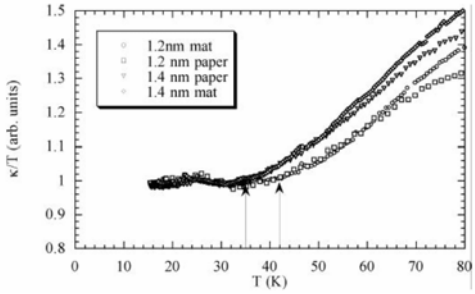
Thermal conductivity of mats of crystalline ropes of SWNTs. RT value of κ deduced ~ 35 W/m·K. (*Hone et al, 1999*). Analysis suggests that phonons dominate thermal transport.



Experimental Data continued: Morphology and Ordering Matter

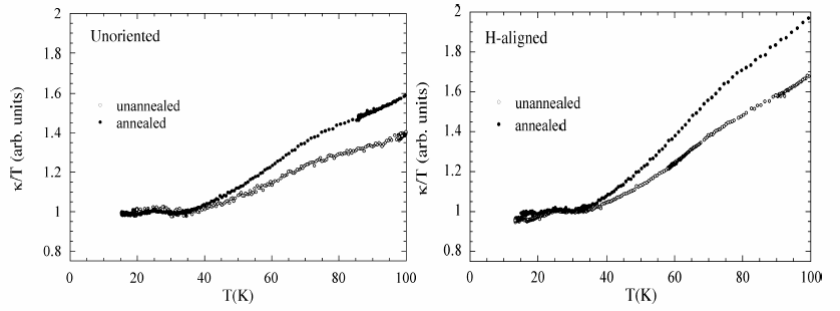


Thermal conductivity of the ‘‘thick’’ annealed sample of aligned SWNT, measured in the parallel direction. At 300 K, κ is much higher than in unaligned material, and is within an order of magnitude of graphite or diamond. (*Hone et al, 2000*)



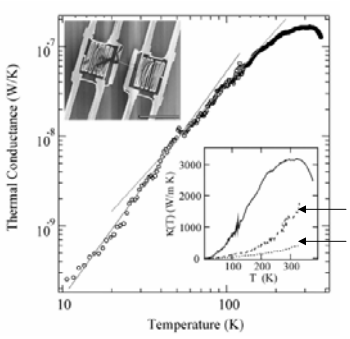
Crossover suggests 1-d quantization is indeed up to higher T for smaller diameters (*Llaguno et al, 2002*)

Morphology Effects (Defects) can be Improved also by additional processing



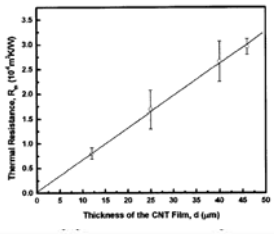
Anneanling helps by eliminating impurities and healing defects (*Llaguno et al, 2002*)

Experimental Data: Multiwall Nanotubes



Individual suspended MWNT (d=14 nm) per *Kim, Shi, Majumdar, and McEuen (2001).* Maximum κ=3000 W/m·K much larger than 20 W/m·K reported for mats (*Yi et al, 1999*). Bundling deteriorates κ.

MWNT films (*Yang et al, 2002*) – noncontact measurements



Tube length (μm)	12	25	40	46
K'_{Air} (W/m K)	268–288	182–243	267–295	250–310
K'_{tube} (W/m K)	13–17	12–16.5	13–17	14–17
Thermal diffusivity α_{tube}(10^{-5} m^2 s^{-1})	1–2.6	1–10	5–9	0.7–1

κ ~ 20 W/m·K deduced independent of tube length. "Taking the volume-filling fraction of CNT's into account, the effective thermal conductivity for the MWNT's is about 200 W/m K".

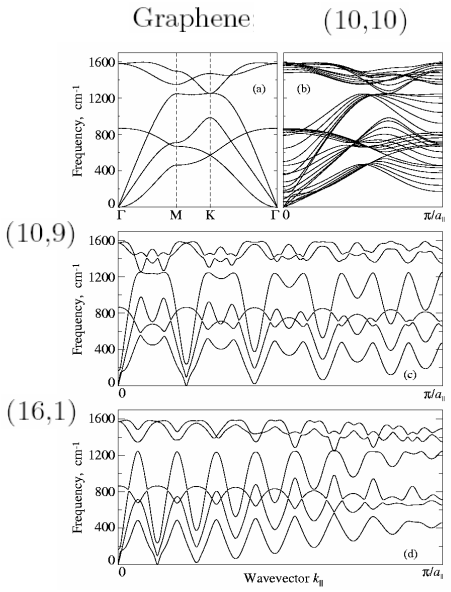
Overall sentiment on experimental situation seems to be that room-temperature values of κ vary from units and tens of W/m·K to a couple of hundred of W/m·K for various arrays, the results ordinarily improving with the decrease of the bundle size. A record result of 3000 W/m·K relates to individual MWNT.

Can this record result have to do with a higher density of layers of the "material" of the sample accompanied by the absence of the need of entangled 3-d heat transfer?

Also, κ seems to be an increasing function of temperature up to about room temperatures.

• Now, what about our understanding of phonons in NTs and the thermal transport?

Model vibrational spectra shown using spiral symmetry

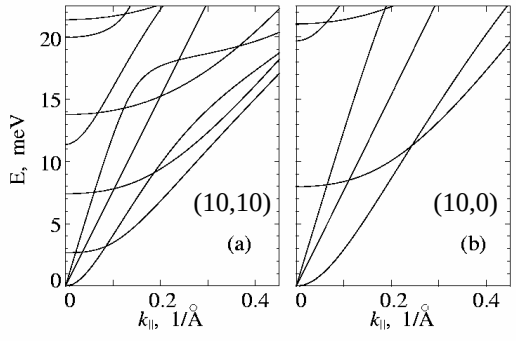


Vibrational spectra of individual SWNTs are basically well understood:

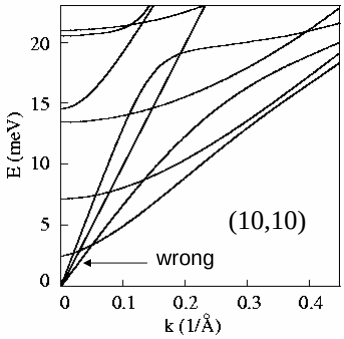
High-frequency part of the spectrum is well represented by zone-folding of the graphene spectrum.

Low-frequency part reflects generic 1-d features common with vibrations of elastic cylinders.

Low-frequency part of the spectrum



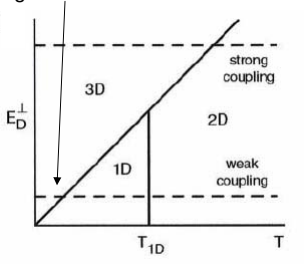
features 4 gapless acoustic modes: longitudinal and twisting with linear dispersion $\omega \sim k$ and degenerate bending with parabolic dispersion $\omega \sim k^2$ as well as higher energy modes with quantized gaps.

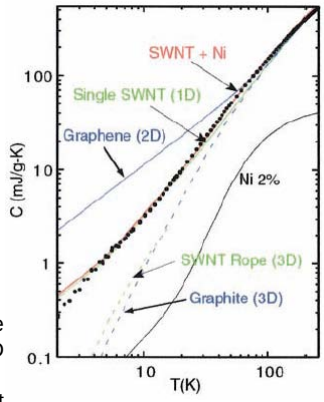


In the "older" picture (however being sometimes used even now) bending (transverse) modes were believed to have $\omega \sim k$.

Intertube Phonon Coupling and Dimensional Crossovers

Experimental data of *Hone et al (2000)* on specific heat in SWNT ropes suggests that intertube phonon coupling is weak.

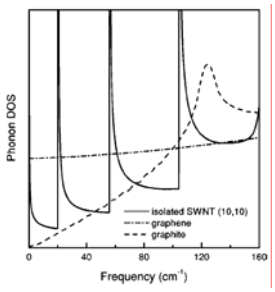




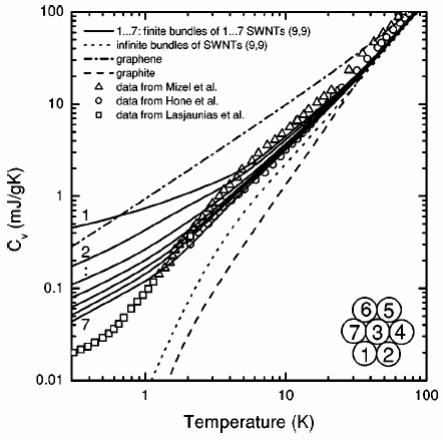
- Isolated tube phonons cross over from a 1D regime where only acoustic subbands are occupied to a 2D regime as higher (optic) subbands are populated.
- In a bundle of weakly coupled tubes, phonons are 3D at very low temperature, then crossing over to a 1D regime.
- If the coupling were strong, the 1D regime would be bypassed and a quantized 1-d phonon spectrum would not be observed.

More accurate analysis of specific heat by *Popov (2002)* does not seem to contradict the conclusion of weak intertube phonon coupling

System	Acoustic branch	Phonon dispersion	Phonon DOS	Specific heat
Graphite	LA, TA	$\omega \propto q$	$D(\omega) \propto \omega^2$	$C_v \propto T^3$
Graphene	LA, TA	$\omega \propto q$	$D(\omega) \propto \omega$	$C_v \propto T^2$
	ZA	$\omega \propto q^2$	$D(\omega) = \text{const}$	$C_v \propto T$
SWNT	LA, TW	$\omega \propto q$	$D(\omega) = \text{const}$	$C_v \propto T$
	TA	$\omega \propto q^2$	$D(\omega) \propto 1/\sqrt{\omega}$	$C_v \propto \sqrt{T}$

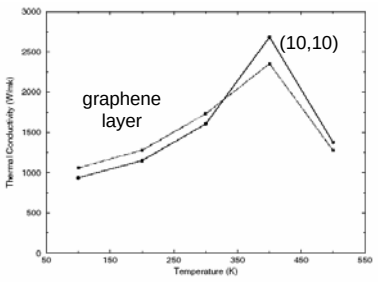


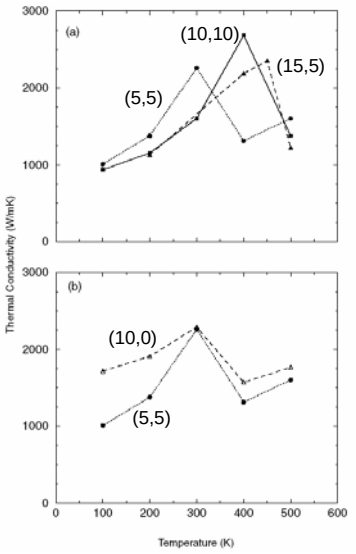
Phonon DOS with correct bending modes



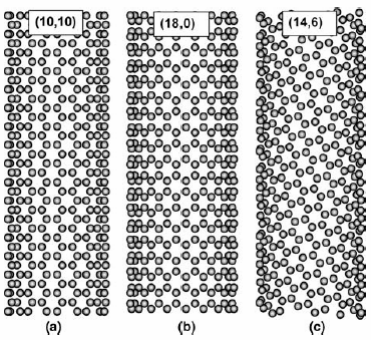
More simulations of thermal conductivity of SWNTs

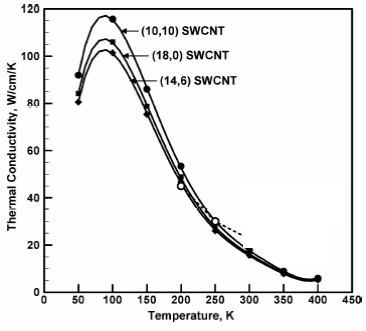
MD simulations of *Osman and Srivastava* (*2001*) also (comp. to Tomanek's) reveal a maximum of κ but of different magnitude and at higher T, and indicate a dependence on tube radius





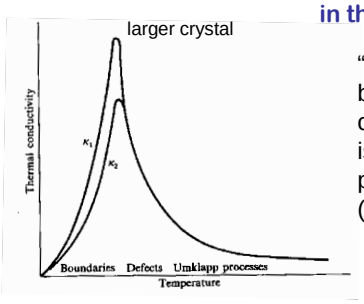
MD simulations of Grujicic, Cao and Roy (2005)





Results are closer to Tomanek's

Despite the variations, MD results show a similar pattern well known in the theory of solids



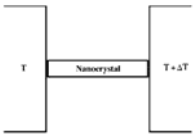
"Between the Umklapp region and the boundary scattering region… the conductivity maximum, whose appearance is perhaps one of the most striking predictions of the quantum theory of solids". (*J. Ziman, 1960*)

Qualitatively, $\kappa \sim C \cdot v \cdot l$

At high T, it is phonon-phonon interactions (umklapp scattering) that reduce mean-free path l.
At low T, umklap processes are not efficient and mean-free path is overtaken by the sample size L. T -dependence is largely that of heat capacity C.

But what is it that plays the role of L in MD simulations, where sample sizes are at best hundreds of angstroms with or without periodic boundaries? Estimates for mean-free paths are normally given as fractions or comparable to a micron. Moreover, one can make simple but fundamental estimates…

Conductance and Conductivity



Conductance G of a "sample": Heat current $J = -G \cdot \Delta T$

Conductivity κ of a "material": Heat current density $j = -\kappa \dfrac{dT}{dx}$

$$\kappa = G \frac{L}{S};\ \text{Length } L, \text{cross-section } S$$

• Additional scatter in reported results is due to various choices of S

Low-T Ballistic Conductance Quantization

(*Rego and Kirczenow, 1998*)

In the absence of phonon interactions (*ballistic*) and for ideal contacts, each acoustic mode in the limit of low T brings quantized contribution to the conductance

$$G_1 = \frac{\pi^2 k_B^2}{3h} T = 9.456 \cdot 10^{-13}\ (\mathrm{W/K^2}) \cdot T;\quad G = N_{\text{channels}} G_1$$

In general, ballistic conductance

$$G = \frac{k_B^2 T}{h} \sum_{\alpha\text{-all monotonic segments}} \int_{Z_{\alpha\,\text{lower}}}^{Z_{\alpha\,\text{upper}}} dx \frac{x^2 e^x}{(e^x - 1)^2};\quad Z = \frac{\hbar\omega}{k_B T}$$

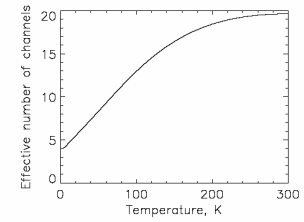
Ballistic conductivity results: A likely upper limit

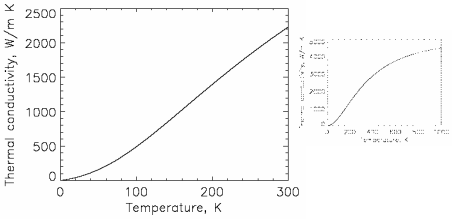
Trying to rationalize MD results, consistency check…:

Knowing vibrational spectrum, it is very easy to calculate ballistic conductance, no other scattering but the boundary one. Here ball. cond. is shown translated into κ for a (10,10) tube, give or take for the accuracy of the spectrum.

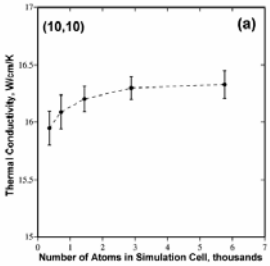
Length used is L=1 micron and cross-section S=250 angstrom^2.

To get, e.g., Tomanek's result at T=100 K, the length would need to be increased by a factor of ~ 80. So what is the meaning of the effective lengths appearing in those MD calculations?

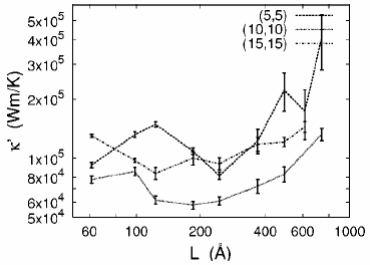




Interesting comments on the convergence of MD results upon the increase of the simulation sample size



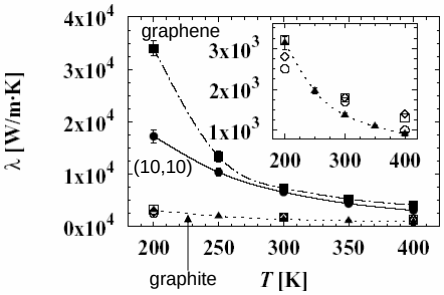
"… despite the fact that the phonon mean free path is considerably larger than the sizes of the computational cells used, an apparent convergence in the thermal conductivity can be obtained". (*Grujicic et al, 2005*)



"We find that the low-frequency vibrational modes of the lattice are limited by the size of simulation domain, and the thermal conductance of an infinite long CNT may be infinite". (*Yao et al, 2005*)

Intertube Phonon Coupling and Thermal Conductivity

Not that much has been done…

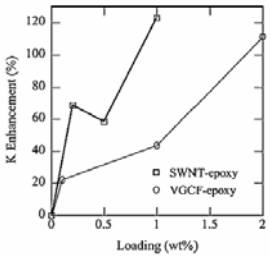


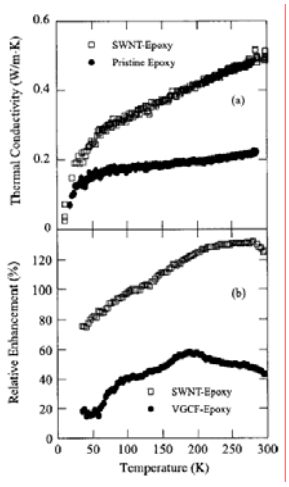
Berber et al (2000) base their conjecture on the analysis of the interlayer effect for graphite:
"Very interesting is the fact that once graphene layers are stacked in graphite, the interlayer interactions quench the thermal conductivity of this system by nearly 1 order of magnitude… We should expect a similar reduction of the thermal conductivity when a nanotube is brought into contact with other systems".

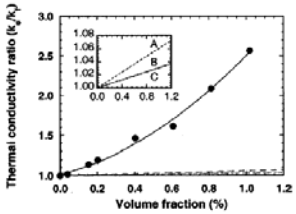
Che, Cagın and Goddard (*2000*): "We also carried out the thermal conductivity calculation for (10, 10) nanotube bundles in close packing condition. The simulations show that the nanotube bundle has very high thermal conductivity along the tube axis, 9.5 W/cm/K [T=300 K], which is comparable to simulated graphite in-plane thermal conductivity, 10 W/cm/K."

Thermal Conductivity Enhancement in Composites

SWNTs in Epoxy
(*Biercuk et al 2002*)



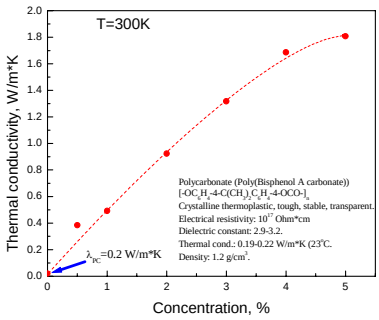




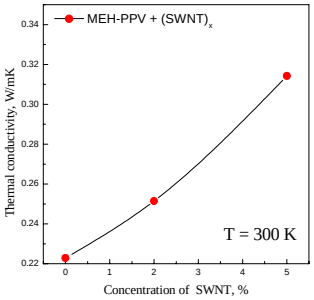
MWNTs in Synthetic Oil
(*Choi et al 2001*)

"In-House" (UTD Nano-Tech) Measurements

(*courtesy of Dr. A. Aliev*)



Substantial enhancement in nearly uniform mixtures of SWNTs in polycarbonate



Much more modest effect for mixtures in conjugated polymer MEH-PPV (attributed to agglomeration of SWNTs).

Effective Medium Analysis for Composites

(*Nan et al, 2003, 2004*)

low volume fraction f result

$$\frac{\kappa_e}{\kappa_m} = 1 + \frac{f \cdot p}{3} \frac{\kappa_c / \kappa_m}{p + \frac{2a_K}{d} \frac{\kappa_c}{\kappa_m}}$$

κ_e - composite

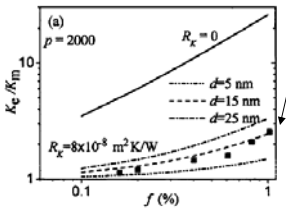
κ_m - matrix

κ_c - nanotube

p - aspect ratio

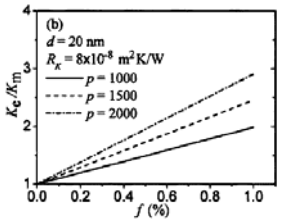
d - nanotube diameter

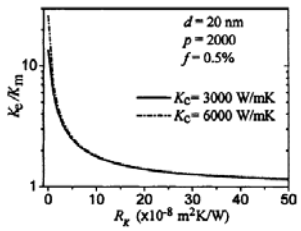
Kapitza radius $a_K = R_K \kappa_m$ due to interfacial thermal resistance R_K



Some exp. data can be rationalized (here κ_c=3000 and κ_m=0.4 W/m·K)

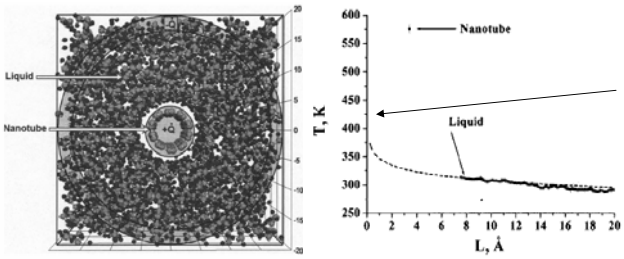
Extremely important role of interface resistance

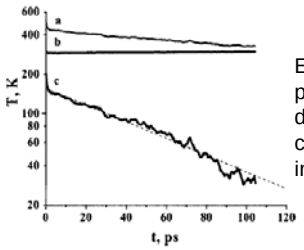




Thermal Interface Resistance between SWNT and octane liquid

(*Cahill and Keblinski's groups, 2003, 2004*)



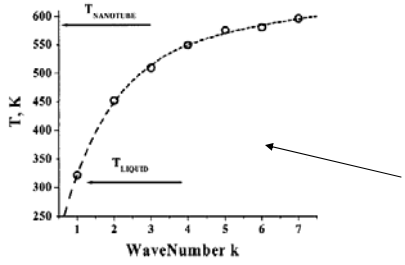


Exponential decay of a pulsed temperature difference leading to a close estimate for interface resistance.

Steady state flow between NT and a sink – local T vs distance from NT.

Dramatic temperature gradient at the interface - *the largest thermal resistance is with the nanotube–liquid interface* estimated to be ~ $3 \cdot 10^{-8}$ m^2K/W for NT ~ 4 nm long and d=0.7 nm. With liquid κ ~ 0.1 W/m·K, the interface resistance is equivalent to having NT surrounded by ~ 5 nm thick extra layer of octane!

Vibrational Mode Analysis of Interface Resistance



Spectral temperature of nanotube bending modes as a function of mode number. The lowest frequency mode has nearly the same temperature as the surrounding fluid while the high frequency modes have temperatures close to the average temperature of the nanotube.

Decrease of the interface resistance with the NT length led to conjecture that it is coupling of low-frequency bending modes of NT to low-frequency octane vibr. modes that provides heat flow – all interactions being driven by dispersion forces (octane-octane and octane-NT).

Spectral temperature analysis confirms.

Shenogin's et al (2004) scenario:

1. The heat energy first flows from the high frequency modes to the low frequency transverse vibration modes (controlled by the intrinsic phonon–phonon scattering in the tube)
2. It then transfers to the layer of octane liquid adjacent to the nanotube (controlled by the coupling between soft modes in the tube and in the liquid)

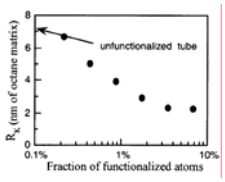
Can Interface Resistance be Decreased by Increasing Coupling to the Matrix? – Yes but only by so much (*Shenogin et al 2004*)

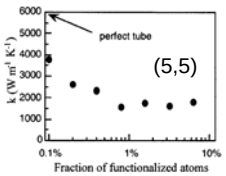
Chemical functionalization – introducing chemical bonds between molecules of matrix (octane) and carbon atoms of nanotube:

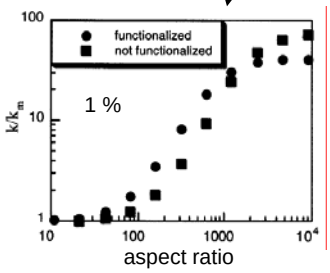
1. Interface resistance IS decreased … but

2. Defects formed on NT decrease its own κ

Net result: A limited improvement by a factor of 2 for a range of aspect ratios







Concluding Remarks

"Modest" applications of nanotubes for thermal management (like 100-200% increase for composites with low conductivity matrices) look quite feasible.

However, in order to evaluate prospects of more aggressive goals fully exploiting the claimed potential, much more research work is needed to provide a firm understanding of issues involved. Among the problems could be:

• Details of the physics of individual tube behavior, especially the low-T regime

• Microscopic picture of intertube/interlayer interactions and scattering

• Microscopic study of contacts with various media (leads)

• Possibility of (self-) assembly of contacts and environments that would be beneficial to the therm. conductivity

• Optimization issues given the understanding achieved